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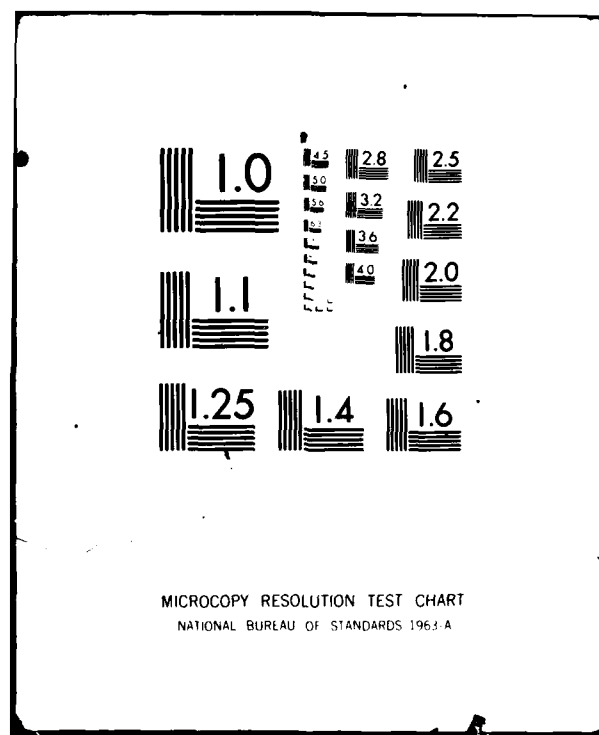
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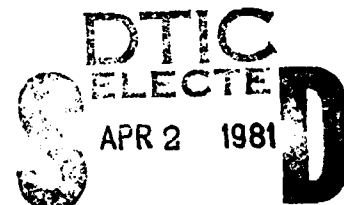
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**REPORT**

**MRL-R-782**

A REVIEW OF SOME PHYSICAL AND CHEMICAL FACTORS AFFECTING  
THE ATTENUATION OF LOW FREQUENCY SOUND IN SEAWATER

Daniel J. Whelan



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REPORT

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ABSTRACT

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- below 0.5 kHz, attenuation is affected predominantly by diffraction and diffusive scattering, but
- in the range 0.5 to 2.5 kHz, it is the effects of chemical relaxation processes, involving boric acid/borate and magnesium/carbonate equilibria, which dominate the sound absorption phenomenon.

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An attempt has been made to trace the contributions of various physical and chemical factors which effect the low frequency attenuation of sound observed in deep ocean channels and to establish that chemical relaxational processes do in fact contribute to the overall attenuation of this sound. The available evidence indicates that :

(i) below 0.5 kHz, attenuation is affected predominantly by diffraction and diffusive scattering, but

(ii) in the range 0.5 to 2.5 kHz, it is the effects of chemical relaxation processes, involving boric acid/borate and magnesium/carbonate equilibria, which dominate the sound absorption phenomenon.

## C O N T E N T S

	<u>Page No.</u>
1. INTRODUCTION	1
2. SOUND CHANNELS	2
3. ACOUSTICAL ATTENUATION AND ABSORPTION LOSS	3
4. ABSORPTION OF LOW FREQUENCY SOUND IN THE OCEAN : THE THORP EQUATION	4
5. PHYSICAL CHARACTERISTICS AFFECTING ACOUSTIC ATTENUATION	5
5.1 <i>Diffraction</i>	5
5.2 <i>Scattering Losses : Oceanic Microstructure</i>	6
5.3 <i>Extraneous Losses and Inteferences</i>	7
6. LOW FREQUENCY SOUND ABSORPTION IN SEA WATER : BORIC ACID	8
7. CONCLUSIONS	10
8. ADDENDUM : A THIRD CHEMICAL RELAXATION PROCESS	11
9. ACKNOWLEDGEMENT	12
10. REFERENCES	12
TABLE 1      VARIATIONS IN THE THORP EQUATION TERMS, OCEAN BY OCEAN	18
TABLE 2      FREQUENCY-INDEPENDENT SCATTERING COEFFICIENTS IN VARIOUS WATER BODIES	19

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# A REVIEW OF SOME PHYSICAL AND CHEMICAL FACTORS AFFECTING THE ATTENUATION OF LOW FREQUENCY SOUND IN SEAWATER

## 1. INTRODUCTION

Sound waves have been used to advantage in the transmission and reception of underwater information for a very long time. In order to appreciate refinements in SONAR techniques, considerable efforts have been made by physicists and engineers [1, 2, 3] and, to a lesser extent, by chemists and biologists, in gaining an insight into factors which affect the attenuation, reflection, refraction and reverberation of sound waves in sea water. In this first paper, it is intended to focus attention on one of these phenomena, that of sound absorption, to review the published literature and to show that the variations observed in the attenuation of acoustical energy by the ocean are influenced both by physical and chemical factors. In a subsequent paper, the effect of oceanographic variables on the principal sound absorbing molecular species will be reviewed. These papers are being presented primarily for the benefit of marine chemists interested in acoustical oceanography, in order to place their work in perspective alongside that of physical oceanographers, physicists and marine engineers.

Particular emphasis will be given to the question of the absorption of *low frequency sound* (<2 kHz) in the ocean as this is an area of considerable current activity, in view of the potential it offers in gleaning underwater intelligence over very large distances.

The first part of the paper will introduce the concept of the *sound channel* and then cover various physical factors which influence the *attenuation of sound* within these channels; the latter part of the paper will be concerned with the interpretation of the frequency-dependent sound absorption parameters in terms of the physico-chemical processes associated with this phenomenon.

## 2. SOUND CHANNELS

The velocity of sound in sea water varies from about  $1450 \text{ m sec}^{-1}$  to about  $1550 \text{ m sec}^{-1}$  at sea level; it increases with increases in temperature, with increases in salinity and with increased pressure (depth) [4].

In the simplest model, changes in typical sound-velocity profiles along a vertical depth in the ocean, below about 100 metres, are governed principally by effects of decreasing temperature with depth; as a result, the profile exhibits a decrease in velocity with depth, perhaps down to depths of about 1500 metres in mid-latitude bodies of water. This is followed by a gradual increase in velocity with greater depth as increasing pressure becomes the dominant variable.

The difference in sound velocity at different depths gives rise to refraction of the sound wave. When velocity decreases with increasing depth, a downward bending occurs; when it increases with depth, there is an upward bending of the sound wave. This refraction of sound gives rise to "shadow zones" and "sound channels" [2].

*Shadow zones* are found in areas of different ocean temperature gradients where one layer, in which there is an upward decrease in sound velocity, occurs above a layer with a downward decrease in sound velocity.

A *sound channel* is caused by a sound-velocity minimum in the velocity-depth profile. Along the axis of this velocity minimum, sound waves are refracted successively upward and downward and are essentially trapped. The sound is constrained to remain in the "channel" and, since the transmission of acoustic energy, particularly at low frequencies, is very efficient, sound within such a channel can be propagated over great distances [5,6].

Urick has analysed the characteristics of two such channels which are regularly encountered in underwater sound propagation experiments in deep water [6], the mixed-layer sound channel and the deep sound channel.

The *mixed-layer sound channel* is a *near-surface channel*; in the top 50 metres of the sea, considerable mixing of waters occurs and the temperature-depth profile shows the presence of an isothermal layer just beneath the surface. Within this layer, the sound velocity increases with depth due to the effect of pressure. Hence, the upward refraction resulting keeps a portion of the acoustic energy emitted by a shallow source close to the sea surface.

The *deep sound channel* usually occurs in a relatively deep water, and originates in the manner described above where the sound velocity profile is a minimum, the effects of decreasing temperature on the sound velocity being compensated by those of increasing pressure. This is the well known *SOFAR* channel (Sound Fixing And Ranging) and the actual depth at which it occurs depends on numerous oceanographic factors determined by the nature and origin of the water masses at a particular location. In mid-latitudes, it typically occurs near 1200 m; in polar regions, it can be near the surface [5,6] - limiting factors at a particular latitude often being the depth of the sea floor and the interaction of various bodies of water. Under ideal

conditions, the SOFAR channel can extend over a very wide range, perhaps in excess of 3000 km.

Over the last two decades, the deep sound channel has been used as an important and popular medium for carrying out underwater acoustic propagation measurements, especially for those involving the transmission and attenuation of low frequency sound (<2 kHz). At these frequencies, attenuation may be only a small fraction of a decibel per kilometer, typically of the order of  $0.1 \text{ dB km}^{-1}$  at 1 kHz. In order to establish a measurable loss, it becomes necessary to use a long propagation path of several hundred kilometers but at the same time to minimise the effects of reflection and scattering losses from the ocean surface and ocean floor; these conditions are often best accommodated in the deep ocean SOFAR channel; hence the interest.

The reduction of data from sound propagation experiments and its subsequent interpretation then require careful consideration of the many factors which effect its transmission, propagation and subsequent reception [6-10]. These include diffusive wave scattering, channel leakage, arising from diffraction, and geometrical spreading, all of which have been modelled mathematically with satisfactory results [11-15].

### 3. ACOUSTICAL ATTENUATION AND ABSORPTION LOSS

The terms "attenuation" and "absorption" are often used interchangeably in the literature but, fortunately, from the context of the discussion, ambiguity seldom arises from this interchange of terms [6,7].

In its broadest sense, "attenuation" is used to include all sound losses resulting from the effects of sound absorption by the medium, by scattering (for example, by marine life, suspended material and undissolved bubbles) and channel leakage.

On the other hand, "absorption" is used to embrace only those processes involving the conversion of acoustical energy into thermal energy and it represents a true loss of acoustic energy to the medium. It covers the frequency-dependent absorptive losses due to viscous absorption of the medium and accompanying chemical relaxations [6,7].

Operationally, the attenuation coefficient,  $\alpha_T$ , is defined by an equation of the form :

$$\alpha_T = \frac{10 (\log I_1 - \log I_2)}{r_2 - r_1} \quad (1)$$

where  $I_1$  is the intensity of the transmitted energy (corrected for spreading losses) at a distance  $r_1$  from the source.

The absorption coefficient,  $\alpha$ , is similarly defined, with regard to that portion of  $\alpha_T$  relating to chemical absorption within the medium.

In oceanographic work under consideration in this review,  $\alpha$  and  $\alpha_T$  are typically quoted in units of decibels per kilometer ( $\text{dB km}^{-1}$ ) or decibels per kiloyard ( $\text{dB kyd}^{-1}$ ). To convert  $\alpha(\text{dB kyd}^{-1})$  to  $\alpha(\text{dB km}^{-1})$  :

$$\alpha(\text{dB km}^{-1}) = \alpha(\text{dB kyd}^{-1}) \times 1.0936 \quad (2)$$

#### 4. ABSORPTION OF LOW FREQUENCY SOUND IN THE OCEAN: THE THORP EQUATION

In the period 1965-1973, a series of communications by Thorp, from the United States Navy Underwater Sound Laboratory, critically examined a wide range of data on the attenuation of acoustical energy in the range 0.1 - 20 kHz. These data originated from deep ocean sound channel experiments and were rationalized [7,16] in terms of the following equation, relating the absorption coefficient,  $\alpha$ , with frequency,  $f$  :

$$\alpha(\text{dB km}^{-1}) = \frac{0.11 f^2}{1 + f^2} + \frac{44 f^2}{4100 + f^2} + 3.0 \times 10^{-4} f^2 \quad (3)$$

where the frequency,  $f$ , is expressed in kHz, (Fig. 1).

These three terms cover the three factors which contribute to the observed sound absorption in *deep ocean channels* at  $4^\circ\text{C}$  over the stated frequency range, namely :

- (i) low frequency relaxation phenomena, probably associated with boric acid-borate equilibria,
- (ii) magnesium sulphate ion-pair absorption, and
- (iii) high frequency relaxation in water, stimulated by resonant changes in shear and volume viscosity.

The evidence for these assignments will be presented later (Section 6) and a fuller description of the Thorp equation, adapting it to describe the absorption of acoustical energy as a function of temperature, salinity and pressure, will be the subject of a separate report from these laboratories.

Recent work, based on laboratory studies [17] and deep ocean experiments [18], has confirmed that the Thorp equation, as given, provides a reasonable first-order description of the dependence of the absorption coefficient,  $\alpha$ , on frequency,  $f$ , but the equation needs to be modified to accommodate the fact that the exact form of this dependence varies from ocean to ocean [17-20] and from water mass to water mass within a particular area [21-25]. This is illustrated in Table 1.

It has been suggested that these variations may originate either from changes in the molecular composition of these water masses in as far as they are influenced by speciation, temperature, pressure and composition [18] or from physiochemical variations alone, e.g. temperature, salinity, etc. [22-25]. The author believes, from the available evidence, that these two factors cannot be separated because variations in temperature, pressure, salinity, etc., do effect concentrations of individual ions and their activity coefficients, the interacting chemical equilibria and the speciation of ions; in other words, changes in one physical variable usually effect changes in the chemical variables.

The real issue is to what extent do these fluctuations (or variations) take place and, more importantly, to what extent do they influence sound attenuation and sound absorption. Large scale fluctuations in temperature, salinity, dissolved gases, etc., inevitably occur over any large water mass extending over a considerable range (several hundred kilometres) [24,25], especially where different ocean masses merge, and these fluctuations will have a marked effect on certain chemical equilibria [18]. On the other hand, small scale fluctuations in temperature, for example, of the order of  $0.05^{\circ}\text{C}$  can occur over a few metres [26-28] and some authors [22-25] suggest changes in acoustic properties may be attributed to these fluctuations, temperature variations which chemists usually note but seldom relate to significant changes in interrelated equilibria.

## 5. PHYSICAL CHARACTERISTICS AFFECTING ACOUSTIC ATTENUATION

As mentioned in Section 3, "absorption" or "absorption loss", as described by the Thorp equation or variations of it, is not always the only factor contributing to the experimentally-observed long-range acoustic attenuation; attenuation can also be enhanced by scattering [11,12] and by diffraction [13-15] of the transmitted sound out of the sound channel.

These effects are often most apparent below 1 kHz and it would appear that their contribution to the magnitude of the overall attenuation can be much greater than that from absorption processes alone [16].

### *5.1 Diffraction*

This is primarily of interest in shallow water.

In shallow water surface ducts, diffraction of very low frequency sound below 0.2 kHz (sometimes much higher) predominates. In this situation, the wavelength of the low frequency sound windows can be too large for refractive trapping to occur, the ocean acts as a coupling medium between the sound source and the earth, rather than as an acoustic trap, and the calculated diffraction effects then far exceed the predicted contribution from absorption effects [11].

Such losses, however, do fall off very quickly as the frequency increases and then become negligible compared to those from other sources [12,13].

The magnitude of these diffraction effects can best be illustrated by two examples from the current literature. In these experiments, attenuation

measurements were carried out in the Gulf of Aden and in the Bismarck Sea [14]. Diffraction effects were then calculated for each ocean mass and these results compared with the measured attenuation.

In the Gulf of Aden, the mixed surface layer duct was relatively narrow (ca. 30 m) and resided over relatively shallow water (50-300 m). At 1.5 kHz, attenuation due to sound diffraction effects was ca. ten times greater than that due to sound absorption and this relative factor increased with decreasing frequency.

In the Bismarck Sea, the mixed surface layer duct was much broader (ca. 90 m), but the depth of the ocean was unspecified (presumably it was ca. 500 m). No measurable diffraction was observed until the frequency decreased to ca. 0.6 kHz, where its magnitude was comparable to the calculated absorption, each ca.  $0.02 \text{ dB km}^{-1}$ . At lower frequencies, the diffraction increased further, while the sound absorption decreased.

In deep ocean channels, calculations indicate that, above 0.1 kHz, diffraction does not contribute to the attenuation [24] to a significant extent.

## 5.2 Scattering Losses : Oceanic Microstructure

While diffraction losses, when they apply, are frequency dependent, scattering loss resulting in dispersion and diffusion of incident sound energy at frequencies above ca. 0.1 kHz appears to be independent of frequency. Mellen, Browning and their collaborators at Naval Underwater Systems Centre [11,12] have calculated the magnitude of these effects on the basis that they arise from randomly distributed inhomogeneities in the temperature and salinity fine structure. These authors have arrived at a formula which relates the observed scattering to known variables, thus :

$$\alpha_s = 8 \times 10^8 \frac{\mu^2}{a_o \Delta z} \quad (4)$$

where (i)  $\alpha_s$  is the excess attenuation due to internal scattering ( $\text{dB km}^{-1}$ ),

(ii)  $\mu^2$  is the variance of the refractive index within the medium,

(iii)  $a_o$  is the correlation distance (metres) describing the path of a sound wave through an oceanographic inhomogeneity [23], and

(iv)  $\Delta z$  is the depth (metres) from the sound channel to the ocean floor.

From a detailed knowledge of the temperature and salinity profiles and the depth of the ocean,  $\alpha_s$  can be evaluated (Table 2) for a particular water mass.

Typical values of  $\alpha_s$  are the order of  $0.02 \text{ dB km}^{-1}$  for shallow waters and of the order of  $0.002 \text{ dB km}^{-1}$  for deep ocean sound channels, indicating

that diffusive scattering losses are comparable with absorptive losses only at frequencies less than 0.5 kHz (shallow waters) or 0.2 kHz (deep ocean sound channels).

The accuracy of the Mellen-Browning model used to arrive at equation 4 is debatable [24,29]; however, it appears to account reasonably for the observed attenuation over and above that calculated using the Thorp equation in a variety of experimental situations by judicious, though reasonable, estimates of the arbitrary parameters used to evaluate  $\alpha_0$ ,  $\mu^2$  and the sound velocity parameters.

An alternative treatment of diffusive scattering has been advanced by Guthrie and aspects of it have been elaborated in simple form by Kibblewhite [29]; it is a more rigorous treatment than that of Mellen and Browning but leads to similar estimates of the excess attenuation due to internal scattering in the SOFAR channel. Guthrie's model varies from that of Mellen and Browning in that it explicitly assumes that the scattering inhomogeneities originate predominantly in the upper part of the oceanic thermocline and should be most evident there, whereas that of Mellen and Browning implicitly assumes a more random distribution of scatterers throughout the sound channel itself.

### 5.3 Extraneous Losses and Interferences

Besides absorption, diffraction and diffusive scattering, several other factors must also be considered, even if prior knowledge or subsequent experiments indicate that they contribute very little to the overall observed attenuation and background noise in a particular frequency range of interest [8].

These factors include the following :

- (i) sound channel leakage [16],
- (ii) boundary losses (both at the water surface and at the bed of the water mass) [6,13],
- (iii) interferences imposed on the intensity and the signature of propagated signals by ambient conditions in the ocean (wind, waves, marine life and sea traffic) [30], and
- (iv) sound absorption and sound scattering from both plant and animal life in the sea [31-33], bubbles [34,35] and particulate matter in the water [36]

and have been reviewed in various sections of the books by Urlick [1,6] and Clay and Medwin [3,37].

Usually these factors are relatively short ranged. In the processing of the experimental data from deep ocean sound channel experiments, it is common to evaluate attenuation coefficients from the slope of a curve representing a plot of an energy function versus a range function, and the author of this paper surmises that the contributions made by these factors can be identified or smoothed out; once this is done the coefficients,

defining the absorption of acoustical energy by chemical relaxation processes, can be evaluated. However, it appears that, even here, much controversy arises and different schools of thought often approach the same problem in their treatment of data in different ways. The results, therefore, are seldom unequivocal [7-10, 38-41].

## 6. LOW FREQUENCY SOUND ABSORPTION IN SEA WATER : BORIC ACID

Although the low frequency attenuation of acoustical energy by sea water attributed to absorption processes is small, of the order of  $0.05 \text{ dB km}^{-1}$  at 500 kHz, and is occasionally much less than the contributions of other processes to the observed attenuation, the author is satisfied that it is real and that it arises from interactions involving boric acid-borate and other equilibria in the ocean.

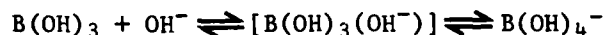
To place this in perspective, one can recall the Thorp equation and the work which it summarizes, as well as acquaint oneself with some of the basic chemistry of boron in sea water.

In sea water of 35% salinity, boron has a concentration of ca.  $4.5 \text{ mg l}^{-1}$  [42]. It occurs principally as inorganic borate,  $\text{B(OH)}_3$ ,  $\text{B(OH)}_4^-$ , and borate complexes [43], only 1-3% of the total boron being associated as organically bound boron [44]. In the form of boric acid in sea water, its  $\text{pK}_a$  varies with temperature, pressure and salinity [45-47]; at 35% salinity and atmospheric pressure, it ranges from 8.86 ( $5^\circ\text{C}$ ) to 8.61 ( $25^\circ\text{C}$ ) [47].

In the period 1940-1955, it was appreciated that sea water exhibits a large excess acoustical absorption at frequencies below 100 kHz and above what is expected from that observed from fresh water. Subsequently, it was established that this excess absorption in the frequency range well above 5 kHz is due to chemical relaxation involving magnesium sulphate ion-pairs [48-53]. In the early sixties, it was further observed that the experimentally determined attenuation below 1 kHz was even greater (5- to 10- fold) than that estimated from magnesium sulphate absorption alone [7,8] and it was suggested that this anomalous attenuation, evident in various deep ocean SOFAR channel measurements, was due to a hitherto unrecognized relaxation phenomenon, with a resonant frequency occurring ca. 1 kHz.

Although the validity of this interpretation was questioned at the time [38] and has remained controversial, much additional work has been carried out, first establishing the basis of the interpretation and then investigating the relative magnitude of this absorption in relation to the overall attenuation, especially in the frequency range below 1 kHz [35].

Recent laboratory measurements [54,55] have identified boron as the key chemical element responsible for this absorption in sea water and indicate that the relaxation process arises from a boric acid-borate equilibrium, simplistically expressed as :



In this equilibrium, the planar trigonal boric acid forms a diffusion controlled ion-pair with the hydroxyl ion which then rearranges to the tetrahedral borate anion; subsequent analyses of the results of these and other experiments indicated that the overall process is accompanied by a large increase in volume,  $\Delta V^0 \approx 36 \text{ cc mole}^{-1}$ .

This relaxation was originally identified on the basis of temperature-jump measurements on standard sea water and synthetic (Lyman-Fleming) sea water, rather than acoustical relaxation techniques; this was necessary because only very small acoustical attenuations were expected and such attenuations could not have been measured with sufficient accuracy using the available resonator techniques, below 5 kHz [54]. It was found that boron-free Lyman-Fleming synthetic sea water did not exhibit any relaxation in the 1 kHz region; however, on addition of sufficient boric acid to duplicate the total boron concentration in standard sea water (ca. 4 ppm), a relaxation process appeared with a relaxation frequency (1.73 kHz, 25°C), similar to that of Copenhagen Standard Sea Water (1971) at the same temperature (1.49 kHz, 25°C).

Additional confirmatory evidence substantiated this assignment. When standard sea water was diluted five-fold with 0.7M sodium chloride solution (with sufficient sodium bicarbonate added to readjust the final pH to 7.66), a shift in the relaxation resonance was observed (0.35 kHz), indicating that the relaxation mode under consideration was concentration dependent and not compensated for by the addition of NaCl-NaHCO<sub>3</sub>. However, on restoring the total boron concentration to that of normal sea water with borax, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, the relaxation resonance reverted to 1.36 kHz, a value close to the original (1.49 kHz).

It is essentially these results which have established the role of boron and its effect on the absorption of low frequency sound in sea water, the main shortcoming in the paper describing these particular experiments being the failure of the authors to report the magnitudes of the observed perturbations in the synthetic sea waters compared to those from the standard sea water.

Since these experiments were reported, Schulkin and Marsh [19] have examined much of the available oceanographic data, carrying out correlation analyses between oceanographic and acoustic variables; their analyses indicate that the acoustical amplitude parameter, "the maximum absorption per wavelength",  $(\alpha\lambda)_{\text{max}}$ , depends exponentially on the pH of the water mass and that the relaxation frequency is related more closely to the salinity (and hence total boron concentration) of the medium than to its temperature, pH or depth. In parallel studies, Browning and Mellen [18,20] and Lovett [10,21] seized upon the fact that variations in the relative amounts of total boron and of boric acid and borate anion are caused by changes in temperature, alkalinity and salinity and thereby rationalize the regional variations which occur in the low frequency attenuation of sound in the various oceans of the world.

These correlations are interesting and important but much laboratory work still needs to be done.

While boric acid is necessary to produce low frequency relaxation and sound absorption, it is not clear to what extent it interacts with other ionic species in sea water nor is it clear how this interaction influences the overall sound absorption [17].

It is well known, that, in sea water, the boric acid-borate equilibrium is coupled with other equilibria; it contributes to the total alkalinity of the medium [56] and borate has the capacity to complex with various metal ions [43,57]. Probably these competing reactions influence the magnitude of the observed low-frequency acoustical absorption for it has been established in laboratory experiments that the dependence of this absorption on the relative concentration of boric acid-borate at constant pH does not follow a simple linear relationship even at the ppm level [17,54]. Hence, any extrapolation to the situation in the ocean must also be complicated.

At much higher concentrations, it is known that boric acid (0.06-0.6M) is in equilibrium with polyborate anions [54] but at the low concentrations of boron in the sea and at the pH of sea water, the relative concentrations of these polyborates should be far too small to account for these anomalies.

Much work has been done on the nature and interaction of borate species in sea water since these initial observations, and the details of this work and its implications will be the subject of a separate report.

## 7. CONCLUSIONS

In this paper, an attempt has been made to trace the contributions of various physical and chemical factors which effect the low frequency attenuation of sound observed in deep ocean channels and to establish that chemical relaxational processes do, in fact, contribute to the overall attenuation of this sound.

To state that there are many problems in studies such as these is to make an understatement and it is not surprising that there are gaps in our knowledge and that the interpretation of the attenuation data from deep ocean sound channel experiments by different investigators does vary.

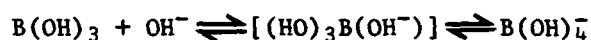
Part of the problem originates in the fact that the ocean is an extremely efficient medium for the transmission of sound and the observed low frequency attenuation and absorption coefficients (Eq. 3) are very, very low. In order to obtain measurable attenuations, it is necessary to study changes in the propagated sound spectrum over extremely long path lengths (often several hundred kilometres); inevitably, the hydrology of the ocean varies considerably over such ranges and due allowance must be made for this factor, inter alia. Subsequent treatment of the experimental data, its analysis and its interpretation then raise further issues as to the relative importance of individual factors in any one situation [7,22-25,39-41].

Despite all of this, a compelling case can still be advanced, establishing that chemical relaxational processes do in fact contribute significantly to the overall acoustic attenuation at frequencies between 0.5-2 kHz and beyond.

Below 0.5 kHz, it appears that diffusive scattering and diffraction processes mask the acoustical absorption effects from chemical processes [11-15,22-25].

In the early fifties, it was established that in the intermediate frequency range, 5-100 kHz, magnesium sulphate absorption contributes significantly to the observed acoustical absorption. However, it was not until the early sixties that sufficient data from low frequency sound absorption experiments had been accumulated and critically examined that a clearer picture emerged, suggesting that additional chemical relaxational processes were probably involved in the absorption of sound below 5 kHz. This work was rationalized in the Thorp equation.

Since then, a compelling story has been put together from the work of Fisher at the Marine Physical Laboratory at the Scripps Oceanographic Institute and his collaborators [17,54]. They have identified the source of this low frequency absorption as arising from boric acid/borate equilibria, but point out that the picture described by the equation :



is much oversimplified and that interactions involving borate-carbonate - pH-metal ion equilibria may all be implicated in determining the magnitude of the overall sound absorption processes in this frequency range. Ion pairs like  $\text{MgHCO}_3^+$  and  $\text{MgB(OH)}_4^+$  [43,58-60] are two entities which may interfere with simple boric acid/borate equilibria in sea water and effect the magnitude of the observed relaxation process or even contribute to them.

Surprisingly, no detailed study has been published on the simplest system,  $\text{B(OH)}_3/\text{B(OH)}_4^-$  in pure water at the low concentrations (4 ppm boron) observed in sea water. Such a study would be expected to yield valuable kinetic data relevant to the whole area of low frequency sound absorption, especially as various ions could then be added systematically and their effects on the observed relaxation frequencies and the intensity of the absorptions noted [61].

In short, a key experiment has been done but it has left many more questions unanswered.

#### 8. ADDENDUM : A THIRD CHEMICAL RELAXATION PROCESS

After this manuscript was completed, the author received a copy of the following preprint :

Mellen, R.H., Simmons, V.P. and Browning, D.G., "Sound Absorption in Sea Water : A Third Chemical Relaxation".

In this work, the authors were investigating the effect of pH on the magnitude of the attenuation of sound in sea water over the frequency range 5-50 kHz, using a spherical acoustic resonator technique.

In short, they found that, over the pH range 8.5-9.0 :

- (i) the observed attenuation was greater at higher pH's (ca. two-fold at pH 9.0) than that predicted on the basis of the modified Thorp equation [17],
- (ii) it could be attributed to an intermediate frequency relaxation ( $f_r = 20$  kHz) involving  $Mg^{2+}/HCO_3^- - CO_3^{2-}$  interactions, and
- (iii) this absorption increases exponentially with pH, is influenced by completing reactions with other ions in sea water ( $Ca^{2+}/CO_3^{2-}$ ,  $Mg^{2+}/SO_4^{2-}$ , etc.), and is temperature dependent.

A fuller appreciation of the contribution of this relaxation process to the total sound absorption is to be included in a forthcoming report, Whelan, D.J. (1979). "Analytical Description of the Sound Absorption Equation", MRL Report, in preparation.

#### 9. ACKNOWLEDGEMENT

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T A B L E 1

VARIATIONS IN THE THORP EQUATION TERMS, OCEAN BY OCEAN

Ocean Area	Temp. °C	Salinity °/oo	pH (mean)	Frequency Absorption Terms (dB km <sup>-1</sup> )	
				Low	Intermediate
Atlantic (30-40°N)	4	35	8.09	$\frac{0.11 f^2}{1 + f^2}$	0.011 f <sup>2</sup>
Pacific (30-40°N)	4	34	7.67	$\frac{0.055 f^2}{1 + f^2}$	0.011 f <sup>2</sup>
Mediterranean	13	38	8.2	$\frac{0.26 f^2}{(1.7)^2 + f^2}$	0.0066 f <sup>2</sup>
Red Sea	22	40	8.16	$\frac{0.20 f^2}{(1.5)^2 + f^2}$	0.0077 f <sup>2</sup>
Gulf of Aden	15	36	7.82	$\frac{0.094 f^2}{(1.2)^2 + f^2}$	0.0066 f <sup>2</sup>
Tasman Sea (SOFAR channel)					
1. Subtropical			7.9	$\frac{0.07 f^2}{1 + f^2}$	0.011 f <sup>2</sup>
2. Aust. Subantarctic				$\frac{0.09 f^2}{1 + f^2}$	0.011 f <sup>2</sup>

References : [18,19,21,25]

T A B L E 2

FREQUENCY-INDEPENDENT SCATTERING COEFFICIENTS IN VARIOUS WATER BODIES

Reference	Water Body	Sound Axis (m)	Water Depth (m)	Scattering Coefficient, $\alpha_s$ (dB km <sup>-1</sup> )	
				Calc.	Obs.
a	Hudson Bay	35	130	0.06	0.04
a	Gulf of Aden	270	1200	0.03	0.02
a,b	L. Superior	145	175	0.2	0.12
a,b	L. Tanganyika	130	750	0.01	0.02
a	Deep Ocean	1000	4000	0.002	
c	Tasman TWO				
	1. Aust. Subantarctic Water				0.002
	2. Subtropical				0.0005
d	South Pacific	(KIWI ONE, 1973)			0.001
d	North Pacific				0.003
e	Baffin Bay	30	2000	0.02	0.02

(a) Ref. 11

(d) Ref. 22

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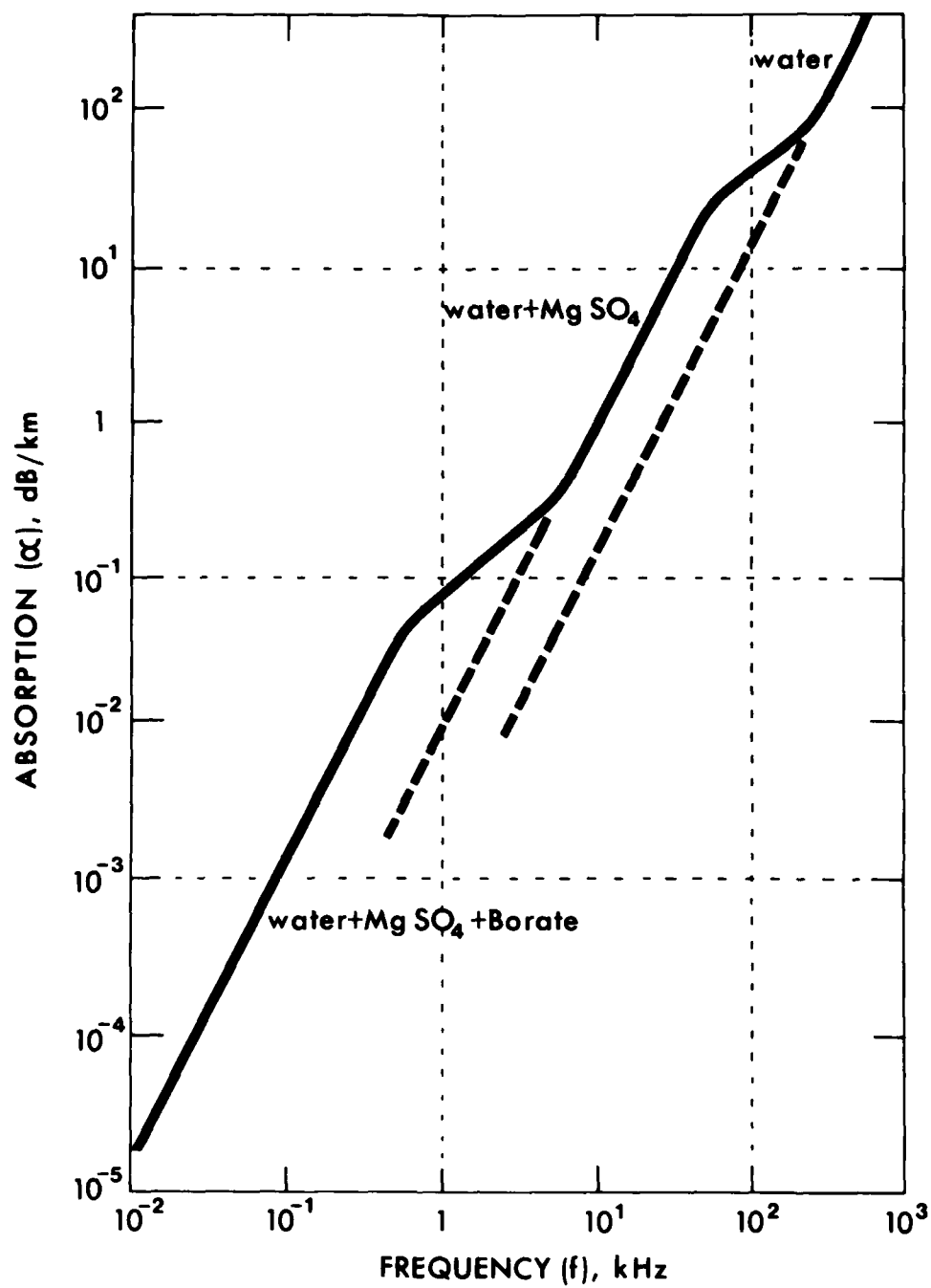


FIG. 1 - Sound absorption in sea water of 35‰ salinity at 4°C, calculated by the Thorp equation (section 4).

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